Activation energies of Si donors in GaN

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The electronic properties of Si donors in heteroepitaxial layers of GaN were investigated. The *n*-type GaN layers were grown by metalorganic chemical vapor deposition and either intentionally doped with Si or unintentionally doped. The samples were evaluated by variable temperature Hall effect measurements and photoluminescence (PL) spectroscopy. For both types of samples the *n*-type conductivity was found to be dominated by a donor with an activation energy between 12 and 17 meV. This donor is attributed to Si atoms substituting for Ga in the GaN lattice (Si_{Ga}). The range of activation energies is due to different levels of donor concentrations and acceptor compensation in our samples. The assignment of a PL signature to a donor–acceptor pair recombination involving the Si donor level as the initial state of the radiative transition yields the position of the optical Si donor level in the GaN bandgap at $\sim E_c-(22\pm4)$ meV. A deeper donor level is also present in our GaN material with an activation energy of ~34 meV which is tentatively assigned to oxygen donors substituting for nitrogen (O_N). © *1996 American Institute of Physics.* [S0003-6951(96)03522-X]

The III–V nitride semiconductors, AlGaInN, have evolved into the materials of choice for the fabrication of visible light emitting diodes exhibiting external quantum efficiencies approaching 10%.[1,2] Controlled *n*-type conductivity is commonly achieved by the incorporation of Si. Si substitutes for Ga in the GaN lattice and acts as a single donor.[3] Despite significant progress, little quantitative information is yet available on the electronic properties of Si donors. Also, the nature of the *n*-type background conductivity observed in most of the epitaxial GaN films is still not fully understood.[4,5]

Si donors in GaN were mainly characterized by variable temperature Hall effect measurements and donor activation energies of ~27 meV are reported in the literature.[6,7] However, these values were derived from Arrhenius analyzes of the measured electron concentration with the implicit assumption of a temperature independent prefactor and, therefore, have a large uncertainty.

To clarify the situation for Si donors in GaN and to investigate the nature of the donors in our unintentionally doped material, we investigated *n*-type GaN films which were either unintentionally doped or Si doped by variable temperature Hall effect measurements and low-temperature (2 K) photoluminescence spectroscopy (PL). The Si content was determined by secondary ion mass spectrometry (SIMS).

The GaN films used in this study were grown by metalorganic chemical vapor deposition (MOCVD) on polished (0001)-oriented sapphire crystals. The unintentionally doped GaN film (sample No. 1) was ~4.5 μm and the Si-doped films (samples Nos. 2–5) were between 2 and 3 μm thick. Sample No. 1 was grown in a different MOCVD reactor than samples Nos. 2–5.

The Hall effect measurements were conducted in the temperature range from 80 to 500 K. The magnetic field was 17.4 kG. Samples of 5×5 mm² size were cut from the wafers and metal dots were vacuum evaporated in the four corners to obtain electrical contacts in the Van der Pauw geometry.

For the PL measurements, the samples were mounted in a cryostat and immersed in pumped, liquid He to achieve a sample temperature of ~2 K. The PL spectra were excited with the 325 nm line of a 30 mW HeCd laser with an incident power density of ~1 W/cm². The resolution of the spectra was 0.05 nm.

Figure 1 presents results from variable temperature Hall effect measurements on an unintentionally doped GaN sample (No. 1). Figure 1(a) shows the electron concentration as a function of reciprocal temperature, and Fig. 1(b) the electron mobility as a function of the temperature. The electron concentration n [Fig. 1(a)] was derived from the experimental Hall constants R_H by:

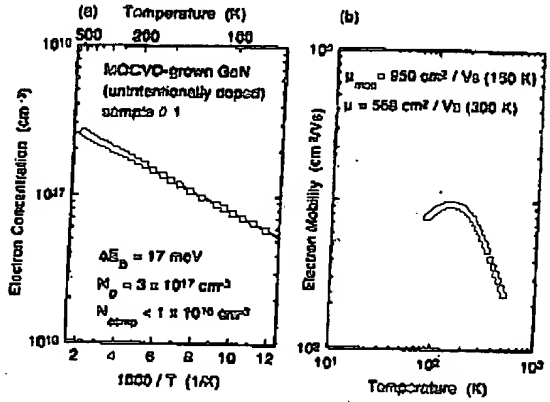

FIG. 1. Electron concentration vs reciprocal temperature (a) and Hall mobility vs temperature (b) for unintentionally doped, *n*-type GaN. The solid squares refer to the experimental data. The solid line in (a) results from a least-squares fit which is described. The fit yields parameters for a shallow donor which are defined as follows: ΔE_D is the activation energy for donor electrons and N_D is the concentration of the donors. N_{comp} is the concentration of compensating acceptors present in the sample.

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fits of the charge neutrality equation to the experimental Hall effect data and results from secondary ion mass spectrometry (SIMS) for n-type GaN samples (column one). The parameter set includes donor electron activation energies (ΔE_{D1}, columns two and four) and concentration of shallow donors (N_{D1}, columns three and five) for two independent donors. Also given is the concentration of compensating acceptors (N_{comp}, column six). SIMS results for the Si content are summarized in column seven.

Sample no.	ΔE_{D1} (meV)	N_{D1} (cm^{-3})	ΔE_{D2} (meV)	N_{D2} (cm^{-3})	N_{comp} (cm^{-3})	[Si] (cm^{-3})
1	17	3.1×10^{17}			$<1\times10^{16}$	4×10^{17}
2	15	1.1×10^{17}	37	3.9×10^{16}	3.2×10^{16}	2×10^{17}
3	14	2.3×10^{17}	34	6.9×10^{16}	$<1\times10^{16}$	5×10^{17}
4	12	7.4×10^{17}	32	6×10^{16}	$<1\times10^{16}$	9×10^{17}
5	-					2×10^{19}

$$n = r_H (q R_H)^{-1}, \tag{1}$$

where r_H is the Hall scattering factor and q the electronic charge. Since r_H has not been measured for GaN it was assumed to be isotropic, temperature independent, and of unity value ($r_H \simeq 1$). In Fig. 1, the experimental data are represented by solid squares. The electron concentration in sample No. 1 gradually increases with temperature.

To obtain information about the donors which determine the electron freeze-out behavior of our unintentionally doped GaN, we performed a least-squares fit of the charge neutrality equation to the experimental data. The charge neutrality equation for n-type, wide band-gap semiconductors (intrinsic carriers are neglected) with M independent donors being given by:[8]

$$n + N_{comp} = \sum_{i=1}^{M} \frac{N_{Di}}{1 + \frac{g_i n}{N_C} \exp\left(\frac{\Delta E_{Di}}{kT}\right)}. \tag{2}$$

where the index i refers to the ith donor: N_{Di} is its concentration, g_i the degeneracy of its electronic state in the band gap (=2), and ΔE_{Di} the thermal activation energy of the donor electrons. N_{comp} is the concentration of compensating acceptors and N_C is the conduction band effective density of states ($=4.3\times10^{14}\ T^{1.5}\ cm^{-3}\ K^{-1.5}$); k is the Boltzmann constant and T the absolute temperature. Fit parameters are ΔE_{Di}, N_{Di}, and N_{comp}. For the fits, an effective electron mass of $0.2m_0$ (m_0=mass of a free electron) was assumed. In Fig. 1(a), the calculated electron concentration as a function of the sample temperature is indicated by the solid straight line. A single donor level describes the electron freezeout behavior and the parameters of the donor level are depicted in Fig. 1(a) and summarized in Table I.

Figure 2 shows Hall effect results for Si-doped GaN samples (Nos. 2–5). The SiH_4 flux during growth was gradually increased from sample Nos. 2–5. Consequently, the electron concentrations increased accordingly as determined by the Hall effect measurements. For samples Nos. 2–4 the experimental Hall effect data were used to obtain information about shallow donors which give rise to the n-type conductivity in Si-doped GaN films by least-squares fits of Eq. (2). For these fits, two independent donor levels had to be employed. Defect parameters are summarized in Table I. The temperature dependence of the electron concentration of

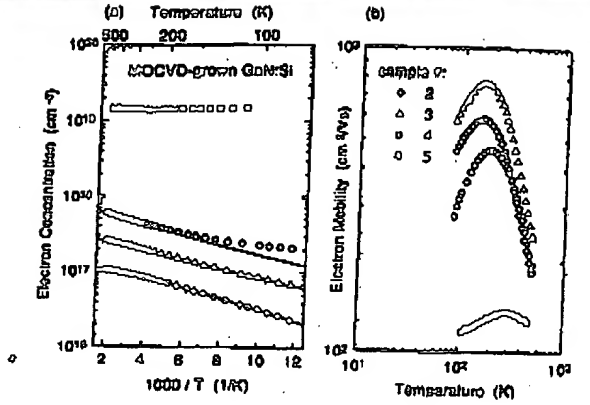

FIG. 2. Electron concentration vs reciprocal temperature (a) and Hall mobility vs temperature (b) for GaN doped with increasing Si concentration. The symbols refer to the experimental data. The solid lines in (a) result from least-squares fits to the experimental data. The fits yield parameters for shallow donors which are summarized in Table I.

sample No. 4 at temperatures below 250 K indicates defect band conduction leading to a deviation of the fitted curve from the experimental data. For sample No. 4 only data above 250 K were used for the fit. The electron concentration of sample No. 5 does not vary with the sample temperature indicating a doping level above the degeneracy limit. The room temperature and the peak mobilities of the Si-doped samples depend on the Si content. Sample No. 2, which has the lowest Si content, has a room-temperature (300 K) mobility of 370 $cm^2/V\,s$ and a peak mobility at 150 K of 582 $cm^2/V\,s$. The highest mobilities for Si-doped material in sample No. 3 with values of 501 $cm^2/V\,s$ (300 K) and 764 $cm^2/V\,s$ (160 K). In sample No. 4 the mobilities are 369 $cm^2/V\,s$ and 459 $cm^2/V\,s$ (190 K). For sample No. 5 the peak mobility is measured at 300 K with 135 $cm^2/V\,s$. The temperature dependence of the mobilities at temperatures higher than the peak mobilities is well approximated by a power dependence $\sim T^{-1.5}$ for all Si-doped GaN films shown in Fig. 2(b) (except sample No. 5).

The Hall effect analysis shows that the n-type conductivity in our unintentionally doped material (sample No. 1) is due to a shallow donor level with an activation energy of ~17 meV (Table I). A donor with a similar activation energy (ΔE_{D1}) is present in samples Nos. 2–4, which were intentionally doped with Si (Table I). The concentration of this donor (N_{D1}) increases according to the flow rates of SiH_4 which was increased from samples Nos. 2–5. Therefore, it seems reasonable to conclude that the shallow donor level with an activation energy in the range between 12 and 17 meV is due to Si incorporation into GaN and that the dominant donor in our unintentionally doped GaN is also Si. Results from secondary ion mass spectrometry (SIMS, Table I) support this conclusion. First, the concentration of Si as determined by SIMS increases according to the concentration of the shallowest donor level (Table I). Second, the atomic concentration of Si is found to be $\sim4\times10^{17}\ cm^{-3}$ in sample No. 1 (Table I).

Our determination of the thermal activation energy for ionization of Si donors is based on an accurate analysis ac-

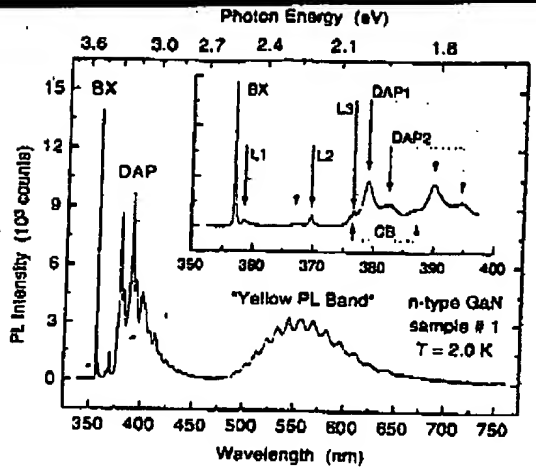

FIG. 3. PL spectrum for sample No. 1. PL emission lines are labeled "BX", "DAP", and "yellow PL band". The inset magnifies the high energy portion of the spectrum. Zero-phonon lines are indicted by arrows with solid lines and their first LO-phonon replicas by arrows with dotted lines. The arrows labeled "CB" indicate a recombination process that may involve the conduction band as the initial state.

cording to the charge neutrality condition, Eq. (2), and yields activation energies ΔE_{D1} in the range between 12 and 17 meV. The decreasing activation energies with increasing donor concentrations observed for samples Nos. 2–4 (Table I) can be explained by interaction of the donor wave functions which reduces ionization energies, as has been observed for other semiconductors, e.g., Si and Ge.[9] However, the unknown Hall scattering factor and its temperature dependence pose an uncertainty in the determination of this value.

The activation energy for donor ionization cannot be determined from variable temperature Hall effect measurements by a slope analysis in a linear region of the electron concentration versus reciprocal temperature data, as demonstrated in Refs. 6 and 7. Such an analysis yields ~4/3 of the actual activation energy as can be shown by a Taylor series analysis of Eq. (2).

A PL spectrum for sample No. 1 is shown in Fig. 3. The spectrum taken at 2 K, exhibits features which are generally observed for *n*-type GaN. The strongest line (BX) appears at 357.0 nm (3.473 eV) with a FWHM of ~2.2 meV. This emission line is due to the annihilation of excitons bound to neutral shallow donors. At lower phonon energies a series of lines labeled DAP is present in the spectrum. In the literature (e.g., Ref. 10), they are usually referred to as due to donor–acceptor recombinations. The yellow luminescence band centered at ~2.2 eV is also present in our material. The inset in Fig. 3 magnifies the high energy portion of the PL spectrum. The PL line labeled "*L1*" is positioned at 358.6 nm (3.458 eV) and is likely to be an acceptor bound exciton. The lines "*L2*" and "*L3*" at 369.7 nm (3.353 eV) and 376.7 nm (3.292 eV), respectively, may indicate Mg contamination since these lines usually appear in our Mg-doped GaN; their origin is unknown. The emission lines labeled "DAP1" and "DAP2" are associated with donor–acceptor pair recombinations and are positioned at 379.0 nm (3.272 eV) and 390.0 nm (3.179 eV), respectively. A broad PL line at (376.4±0.4) nm [(3.294±0.004) eV] is labeled "CB".

In the following, we use the PL emission lines "CB" and "DAP1" to suggest the positions of the Si donor level and the Mg acceptor in the GaN band gap. DAP1 is the highest energy line and, therefore, should involve the shallowest donors and acceptors, namely Si and Mg. We assume that the broad line "CB" is due to the same radiative transition, however, with the initial state being the conduction band edge. The energy difference between the CB and the DAP1 line yields the position of the Si donor level at $E_c-(22\pm4)$ meV. Consequently, the optical level for the Mg acceptors follows at $E_v+(209\pm5)$ meV [$E_{gap}=(3.503\pm0.0005)$ eV, 2 K].[11]

A second donor level with electron activation energies (ΔE_{D2}) between 32 and 37 meV is observed in samples Nos. 2–4 (Table I). This donor level may be due to oxygen contamination. Oxygen substituting for nitrogen has been suggested to act as a shallow donor and may contribute to the *n*-type background conductivity in unintentionally doped GaN.[5]

In conclusion, we have determined the activation energy for ionization of Si donors in GaN by variable temperature Hall effect measurements. For the samples investigated in this study, the analysis yields activation energies in the range between 12 and 17 meV. Therefore, and due to its high solubility in GaN Si is well suited as a donor dopant for the preparation of *n*-type GaN layers with electron concentrations in the range up to $\sim 10^{20}$ cm^{-3}.

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